



Article

Formic Acid Manufacture: Carbon Dioxide Utilization Alternatives

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Abstract: Carbon dioxide (CO₂) utilization alternatives for manufacturing formic acid (FA) such as electrochemical reduction (ER) or homogeneous catalysis of CO₂ and H₂ could be efficient options for developing more environmentally-friendly production alternatives to FA fossil-dependant production. However, these alternatives are currently found at different technological readiness levels (TRLs), and some remaining technical challenges need to be overcome to achieve at least carbon-even FA compared to the commercial process, especially ER of CO₂, which is still farther from its industrial application. The main technical limitations inherited by FA production by ER are the low FA concentration achieved and the high overpotentials required, which involve high consumptions of energy (ER cell) and steam (distillation). In this study, a comparison in terms of carbon footprints (CF) using the Life Cycle Assessment (LCA) tool was done to evaluate the potential technological challenges assuring the environmental competitiveness of the FA production by ER of CO₂. The CF of the FA conventional production were used as a benchmark, as well as the CF of a simulated plant based on homogeneous catalysts of CO₂ and H₂ (found closer to be commercial). Renewable energy utilization as PV solar for the reaction is essential to achieve a carbon-even product; however, the CF benefits are still negligible due to the enormous contribution of the steam produced by natural gas (purification stage). Some ER reactor configurations, plus a recirculation mode, could achieve an even CF versus commercial process. It was demonstrated that the ER alternatives could lead to lower natural resources consumption (mainly, natural gas and heavy fuel oil) compared to the commercial process, which is a noticeable advantage in environmental sustainability terms.

Keywords: carbon capture and utilization; formic acid; life cycle assessment; electrochemical reduction

1. Introduction

Formic acid (FA) is a valuable chemical product that is difficult to replace in certain applications. Its strong acidic and reducing properties make it useful in agriculture, pharmaceuticals, food, textiles, and chemicals. FA has recently been suggested as a promising hydrogen storage component via its decomposition to CO₂ and H₂ with a possible reversible transformation back to regenerate formic acid, which serves as a platform for chemical energy storage [1]. The conventional production processes of FA are based mainly on fossil fuels utilization. Production processes of formic acid can be classified into four groups: methyl formate hydrolysis, oxidation of hydrocarbons, hydrolysis of formamide, and preparation of formic acid from formates. Among them, the methyl formate-based process route is currently dominant [2]. Worldwide formic acid production capacity by hydrolysis of methyl formate was estimated at 770 kton·year^{−1} in 2014, covering approximately 90% of the overall installed capacity. This process involves a carbonylation of methanol and subsequent hydrolysis of the methyl formate that is produced.

Carbon dioxide (CO₂) emissions during the production of FA that use hydrolysis of methyl formate came from the required steam and syngas productions in the upstream processing. Syngas is needed as CO in order to react with methanol; it may come from steam reforming of light ends, as natural gas, from partial oxidation of fossil feedstocks or from coal gasification [3]. Limitations of the FA conventional process can include slow reaction rate, undesirable by-products, high cost of investment, and issues related to the environment such as the high energy requirements (in the separation stage) and a noticeable dependence on fossil fuel (heavy fuel oil is used in the synthesis of CO) [4]. Thus, in parallel to the alarming issue of the global warming and climate change, the depletion of the mentioned fossil fuels, which must remain underground for generations to come, may seem less evident. Therefore, it is not surprising that nowadays the utilization of CO₂ is gaining momentum in the scientific community and the industrial corporations in order to shift from conventional fossil-based processes toward environmentally-friendly processes.

In that context, CO₂ could be a feedstock for the production of a wide variety of fuels and commodities including FA. The concept, known as CO₂ valorisation, offers a potential solution directed towards the pursuit of mitigation targets set by the COP21 Paris Agreement to abate the problem of the greenhouse effect [5]. Undoubtedly, it cannot be claimed that climate change will be solved merely by the utilization of CO₂ to FA or any other reduced form of CO₂ such as methanol, syngas, methane, ethylene, etc., but the exploration of new alternatives to fossil-based production routes shows a potential pathway with which to contribute to the curbing of CO₂ emissions.

Some of the main available processes to convert CO₂ into FA are homogeneous catalysis [6–8], heterogeneous catalysis [9–12], photocatalytic reduction [13], and electrochemical reduction (ER) [14,15], which share a substantial input of energy per unit of reduced CO₂ [6]. These CO₂ utilization technologies for production of FA are currently found at different stages in terms of maturity. The alternatives should be economically viable, safe, and sustainable for their final industrial commercialization. The efforts are mainly focused on decreasing the overall energy consumption of the processes. On one hand, thermocatalytic synthesis of FA from CO₂ and H₂ may be easily adopted due to it being based on currently available technology; however, it needs a high heat input or a heat integration [7]. Another approach is the photocatalytic method that could use visible light directly [13], avoiding the associated carbon footprint of the energy conversion that it is still found at lower TRLs. On the other hand, ER of CO₂ is still behind in terms of TRLs compared to catalytic ways but has the advantage that it can be fully developed at atmospheric temperature and pressure in such a way that it can utilize surpluses of electricity from renewable sources [16,17]. Despite the numerous advances and novel approaches in recent decades, the ER process remains challenging because of (i) the high overpotential needed, (ii) the high consumption of steam of the final separation step, (iii) the low solubility of CO₂ at both ambient temperature and pressure, and (iv) the deactivation and damage of the electrodes [18]. Continuous efforts are still required to achieve an efficient ER of CO₂ from the point of view of environmental sustainability. The development of highly active and durable electrocatalysts for both the cathode (CO₂ reduction reaction) and the anode (O₂ evolution reaction), as well as electrodes and electrolytes that have high conductivity and allow for sufficient mass transport of the reactants and products to/from the catalyst layers, are some of the key points to ensure environmental sustainability [19,20].

A recent economic-viability study of four possible routes for the ER of CO₂ to liquid products (including FA) has demonstrated that the primary economic limiting factor is the high capital expense for the electrolyzer units [21]. Consequently, some technological challenges need to be overtaken to make ER alternative an industrial viable option. It is clear that several options are available and, at least, environmental sustainability must be analysed prior to any other economic or social consideration. In this study, Life Cycle Assessment (LCA) is used as a decision-making tool for process development, enabling the prediction of the sustainability implications of the different alternatives. LCA is a widely used tool that is used to evaluate the net contribution of the use of carbon dioxide [22–25], and thus it can be used to compare the FA conventional process with both CO₂ utilization alternatives.

In a previous study from the authors, it was concluded that the integration of renewable energy was required to ensure the potential environmental sustainability of FA by ER synthesis based on the champion lab data at the time of the study [26]. The results obtained in this study provide a complete overview of the remaining technological challenges, especially for the competitiveness of CO₂ utilization plants based on ER as it remains in its infancy. The technological aspects included in this study involve (1) reaction, by means of the concentration of FA at the outlet stream of the ER cell, the cell voltage, the faradic efficiency, and the mode of operation (i.e., recirculation); and (2) the separation step, by means of azeotropic distillation.

This work aims to compare, in terms of carbon footprint, the FA commercial production process (fossil-based) with two of the main CO₂ utilization alternatives of FA synthesis (homogeneous catalysts and the novel ER of CO₂) based on the latest available experimental developments [7,14,15]. Savings in terms of raw materials are also included for a more fair comparison. The novelty of this work relies on the use of new champion lab data, which show the tremendous progress taking place in the ER research field in order to check if current technological developments can even out the conventional production processes in terms of carbon footprint.

2. Methodology

A comparison of three options for the production of 1 kg of FA at commercial concentration of 85% wt. (Figure 1) was completed in terms of carbon footprints (CFs). The FA manufacture options consist of two CO₂ utilization alternatives (based on ER of CO₂ and homogeneous catalysis of CO₂ and H₂) and a third one as benchmark in the form of the commercial conventional process. CFs were determined by means of the LCA tool (cradle-to-gate approach). The CF assessment of the alternative based on a ER of CO₂ (A_{ER}) was performed using the experimental data of three selected available studies generating three ER scenarios labelled as A1.1, A1.2, and A1.3 [7,14,15]. A1.1 represents the current best performance within the research group of the authors. A1.2 and A1.3 represent the best champion data available in the literature regarding FA production by ER in terms of concentration. Their estimated values of CF were then compared with those CF values corresponding to the FA conventional (A_{CONV}) process [27] and the simulated CO₂ utilization alternative based on homogeneous catalysis of CO₂ and H₂, which was found in the literature (A_{JCR}) [6]. On one hand, a comparison between the CF values of the three novel ER alternatives (A1.1, A1.2, and A1.3) and the CF of A_{CONV} was performed in order to provide an overview of the main remaining challenges to achieve at least carbon neutral cycle of FA production by ER (which is still in development) compared to the conventional route. On the other hand, the comparison of the results with the better-known A_{JCR} alternative was included in the study in order to reflect the different levels of development and their viabilities for a final industrial competitiveness. Additionally an assessment of the amount of raw materials needed in both CO₂ utilization alternatives and the conventional process was done to evaluate mainly the fossil fuel savings. The functional unit used in the study is defined as 1 kg of FA at a commercial concentration of 85% wt. Ecoinvent 3.3 database [27] and GaBi Professional software [28] were used in the background process.

2.1. Alternative Based on Electrochemical Reduction CO₂

To estimate the CF of the ER alternatives A1.1, A1.2, and A1.3, the LCA system framework was set as in Figure 2. As it can be seen, there are three main steps: the ER of CO₂, the distillation of the products, and the compression of parallel obtained byproducts such as H₂ and O₂ in a liquid form ready to transport. Energy consumption is in the form of electricity or steam according to the nature of each individual process.

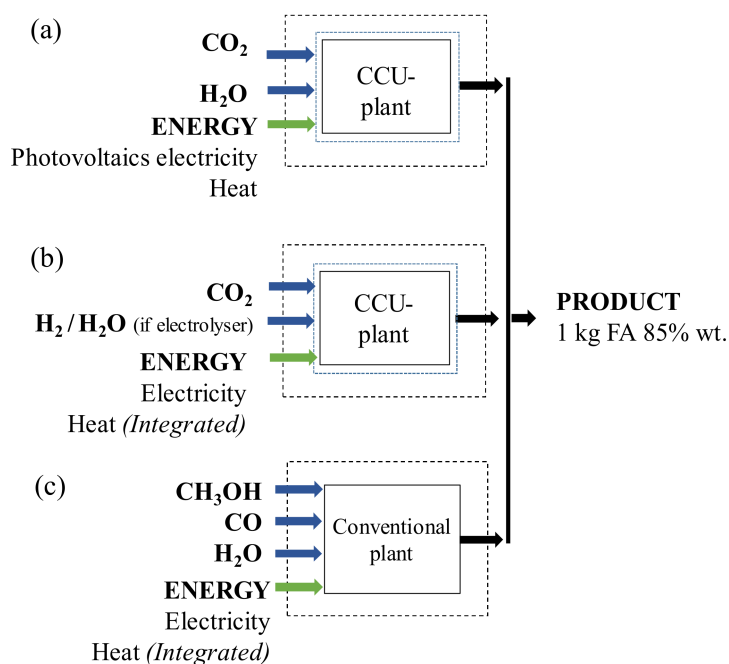


Figure 1. System frameworks: (a) alternative A_{ER} (scenarios A1.1, A1.2 and A1.3), (b) alternative A_{JRC} , and (c) conventional A_{CONV} .

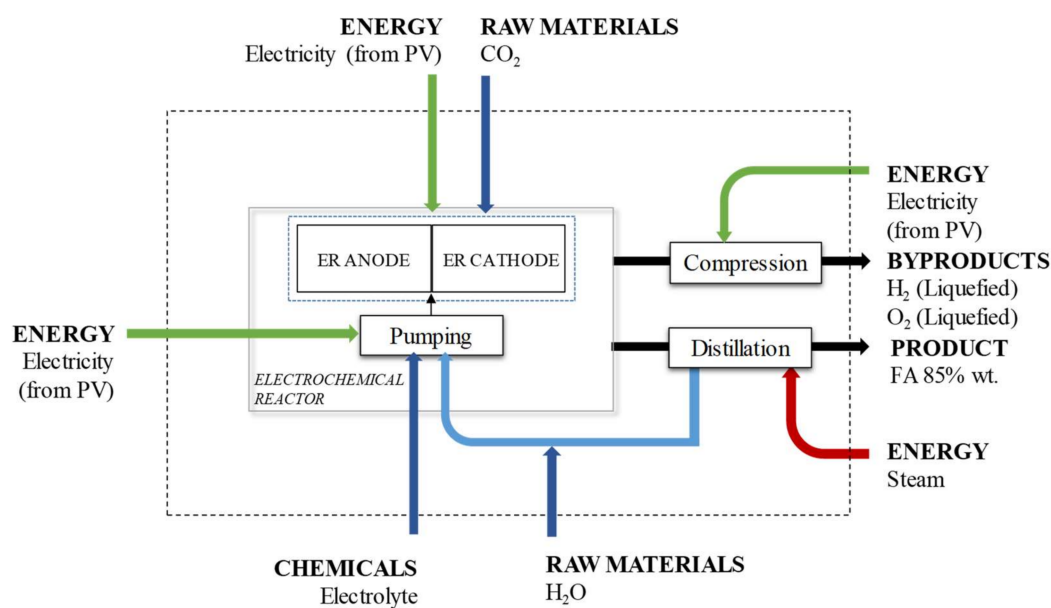


Figure 2. CCU system framework.

Mass balances are based on the reaction of the CO_2 ER shown in Table 1, assuming neutral to alkaline conditions [29,30]. CO_2 and water are injected in the cathode. As solubility of CO_2 is assumed to be very high, the soluble CO_2 reaches the cathode surface. CO_2 is reduced to formate ($HCOO^-$) and H_2O to hydroxide ions (OH^-) in the presence of the correspondent electrolyte in the cathodic compartment of the ER cell. Simultaneously, the formation of oxygen (O_2) and protons (H^+) is considered as the only reaction taking place in the anodic compartment. Both the formate ions and hydroxide ions migrate to the centre compartment through the membrane, where they balance the protons produced in the anode to form FA ($HCOOH$) and water (H_2O). In an ideal ER reactor, an excellent electrode would lead to a value of 100% for the faradaic current efficiency (FE). This would

correspond to the formation of pure HCOOH in the cathode and pure O₂ in the anode. However, a part of the applied current density is deviated to other parallel/parasitic reactions [30], reducing the FE to FA production. In this study, H₂ evolution reaction (HER) is assumed as the unique parallel reaction. It is considered that water is the chemical compound that is consumed regardless of the pH in the half-cell being acid or basic. The O₂ evolution reaction (OER) is the only reaction taking place in the anode.

Table 1. Main and side reactions.

Cathodic Reaction	Anodic Reaction
$\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HCOO}^- + \text{OH}^-$	$\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{e}^- + 1/2 \text{O}_2$
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$	
Overall reaction	
$\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{O}_2 + \text{H}_2$	

A purification process in the form of a distillation is required to increase the FA concentration at the outlet of ER to the accepted commercial concentration value at 85% wt. Therefore, cooling and heating are needed. The distillation process was simulated in a previous study carried out by the authors [26]. The simulation considers only presence of water (obtained as a head product) and FA (obtained as the bottom product) at the required concentration. Distilled water is recirculated and reinjected to the inlet freshwater stream to the cathode. Then, net water consumption is the difference between water in the inlet stream and water that is recirculated. The pure O₂ produced as a secondary product, mainly by the anodic reaction, is separated, liquefied, and recovered, as well as H₂, which is produced by the competing reaction, and it is assumed to be pure.

Finally, a summary of additional hypothesis that was taking into account in this work is listed next:

- A CO₂ valorisation plant is in the same site of the CO₂ source (no transport is required).
- The feed of CO₂ to the plant is assumed to be pure and with a suitable pressure for the ER process.
- The feed of CO₂ to the plant is assumed to be free of environmental burdens. The feedstock CO₂ sourced to the plant is for free, so 100% of the burdens are allocated to the product that directly releases the CO₂, e.g., electricity forms a coal-fired power plant.
- The vapour steam needed for FA purification exists in dry saturated conditions.
- Electrolytes used in the ER process can be perfectly separated and they are considered to be avoided products.
- The lifetimes of the electrode materials and catalysts are long enough to neglect their carbon footprint.

Life Cycle Inventory (LCI) and LCA (cradle-to-gate analysis) were performed based on the experimental conditions used in three different approaches of ER of CO₂ to formate/formic acid that were found in the literature. The selected references and their corresponding conditions are summarized in Table 2. Data for A1.1 was obtained within the research group of the authors [15]. This work represents a relevant advance compared to previous results due to the high concentrations obtained. A1.2 and A1.3 are, to the best of our knowledge, the performing champions in terms of FA concentration. This way, it is possible to establish a benchmark for further developments as later discussed. A1.2 and A1.3 [14] alternatives were selected because of their demonstrated capability of producing FA concentrations of 10.0% wt. and 20.5% wt., respectively. Main difference between A1.2 and A1.3 is their mode of operation, being single pass in the case of A1.2 (as in the case of A1.1) and recirculated mode in the case of A1.3. Electrolyte flowrate used in A1.1 reference is an order of magnitude higher than A1.2 and A1.3. Differences in electrode and membrane materials can be also observed. They share mainly the cathode material in the form of Sn nanoparticles (Sn NPs) deposited over a carbonaceous GDE. Regarding FE, A1.1 shows a higher value than A1.3 but is lower than A1.2.

Catalytic electrode materials, reactor design, hydrodynamic conditions, current density, supporting electrolyte, etc., could be potentially combined to yield the best FE.

Table 2. Experimental conditions of the selected references/scenarios for the carbon footprint of CO₂ to formic acid.

	UNITS	A1.1 [15]	A1.2 [14]	A1.3 [14]
Cathode		Sn NPs (Sn/C-GDEs)	Sn NPs (Sn/C-GDEs)	Sn NPs (Sn/C-GDEs)
Anode		DSA/O ₂ (Ir- MMO on Pt)	IrO ₂ on Toray paper	IrO ₂ on Toray paper
Cation membrane material			Dupont Nafion 324	Dupont Nafion 324
Anion membrane material			Dioxide Materials Sustanion™	Dioxide Materials Sustanion™
Current density, i	mA·cm ⁻²	200	140	140
Electrolyte flowrate to geometric projected cathodic area, Q/A	mL·min ⁻¹ ·cm ⁻² (10 ⁻³)	70.0	6.00	6.00
Geometric projected cathodic area, A	cm ²	10.0	5.00	5.00
Faradaic current efficiency, FE	%	42.3	94.0	32.0
FA reaction rate, r_{FA}	mmol·m ⁻² ·s ⁻¹	4.38	2.22	4.63
Overall cell voltage, E_{cell}	V	4.30	3.28	3.28
Concentration of FA, [FA]	% wt.	1.68	10.0	20.5
Mode of operation		Single pass	Single pass	Recirculated

The detailed LCIs for required materials and energy corresponding to each set of experimental data were calculated by means of a sequence of energy and mass balances. More details can be found in the supplementary data published in a previous study [26]. Mass balances were performed in each unit, ensuring that there were no mass losses for any element. This methodology ensures that each CCU-ER alternative is treated equally; thus, the results are directly comparable. The electricity needed in the process, such as the electricity demanded in the reduction of CO₂ to FA, the electricity for the pumps within the reactor cell, and the electricity needed for liquefying both O₂ and H₂, was assumed to come from the surplus production of renewable energy in the form of photovoltaic solar energy (PV). Alternatively, wind power could be also considered. Surplus energy derives from avoiding curtailment of PV solar or wind farms due to the possibility of injecting excess power in the CCU facility. The periods in which the electricity generation exceeds the demand create a problem of “surplus production”, which can help at the ER of CO₂. This selection determines the CF of each unit of electricity used for the process, which in this case was 0.03 kg·kWh⁻¹ [31]. The use of other high-carbon source for the electricity consumption will make no sense for ER purposes [26]. Pumping needs are derived from the need to overcome the pressure drop inside the reactors. Heat, as steam, is a utility used in the distillation unit. The source for this steam is natural gas and the CF per unit of steam used is 0.277 kg·kg⁻¹, which was obtained from Ecoinvent data [27].

2.2. Alternative Based on Homogeneous Catalysts of CO₂ and H₂ (A_{JCR})

The CCU alternative labelled as A_{JRC} displayed a CF per unit mass of FA as low as 0.166 kg·kg⁻¹ supported by a set of hypothesis [7]. The main hypothesis is (i) hydrogen needed by the A_{JRC} plant is supplied by water electrolysis, (ii) the CO₂ use and capture plants are at the same site (no transport is needed), and (iii) the compression of CO₂ from atmospheric pressure to the pressure of the synthesis process is allocated to the utilisation plant [7].

2.3. Conventional Production of Formic Acid (A_{CONV})

Conventional FA manufacture was assumed by means of hydrolysis of methyl formate. This route consists on a two-stage process: in the first stage, methanol is carbonylated with carbon monoxide (CH₃OH + CO → HCOOCH₃), and in a second stage, methyl formate is hydrolysed to FA and

methanol ($\text{CH}_3\text{OOCH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCOOH}$). The CF of FA conventional process, as kg of CO_2 per kg of FA produced is $2.2 \text{ kg} \cdot \text{kg}^{-1}$, which was obtained from Ecoinvent data [27]. This CF value could decrease up to $2.07 \text{ kg} \cdot \text{kg}^{-1}$ whether PV solar was supplied to a FA conventional plant instead electricity from the production mix.

3. Results and Discussions

3.1. Life Cycle Inventory of the Selected Alternatives and the Conventional Production Process

Table 3 shows a summary of the LCI results obtained at the outlet of the ER process assuming a final concentration of FA at the bottom of the distillation column of 85% wt. for A1.1, A1.2, and A1.3 as ER processes. Additionally, there are summarized values related to the commercial route of production sourced from Ecoinvent [27] (A_{CONV}) and the alternative of the direct catalytic reaction of CO_2 and H_2 (A_{JRC}). The values summarized in Table 3 are grouped as electrode/catalyst materials, raw materials, products (formic acid 85% wt.), other valuable products obtained in the process (H_2 and O_2), and energy and heat demand (steam). This study considers that other salts and acids used in ER process can be perfectly recirculated.

Table 3. LCI for the ER of CO_2 according to the three selected experimental data references (A1.1, A1.2, and A1.3), the conventional commercial process sourced from Ecoinvent [27] (A_{CONV}), and an alternative CCU process based on the catalytic conversion of CO_2 and H_2 [7] (A_{JRC}). The functional unit is 1 kg FA.

	UNITS	A_{ER}			A_{JRC}	A_{CONV}
		A1.1	A1.2	A1.3		
Electrode/Catalyst						
TOTAL	$\text{kg} (10^{-6})$	1.30	9.92	14.9	3.75	15.60
Raw materials						
CO_2	kg	0.95	0.96	0.96	0.83	-
H_2O	kg	1.10	0.59	1.41	0.56	0.60
CO	kg	-	-	-	-	0.61
CH_3OH	kg	-	-	-	-	0.04
Products						
HCOOH	kg	1.00	1.00	1.00	1.00	1.00
H_2O	kg	0.18	0.18	0.18	0.06	0.18
By-products						
H_2	$\text{kg} (10^{-3})$	59.00	3.00	92.00	-0.06	-
O_2	kg	0.82	0.37	1.09	0.48	-
Energy						
Electricity						
ER	kWh	11.80	4.59	11.93	-	-
Pump	$\text{kWh} (10^{-3})$	7.35	1.24	0.63	-	-
Compression	kWh	0.15	0.04	0.11	-	-
TOTAL		11.80	4.59	11.90	4.07	0.29
Heat demand						
Steam	MJ	401.00	65.18	25.67	10.03	22.77

It can be seen in Table 3 that values of ER energy and steam are expected to be the main resources contributing to the overall CF. The electricity consumption by ER per mass unit of FA ranges between $4.59 \text{ kWh} \cdot \text{kg}^{-1}$ and $11.93 \text{ kWh} \cdot \text{kg}^{-1}$, with A1.2 alternative having the best conditions in terms of electric consumption. The differences are mainly due to the combinations of reaction rates and cell potentials at a certain current density. A1.2 has the lowest flow rate (for pumping) and the highest Faradaic Efficiency. These values are well over the minimum theoretical electricity consumption of $1.72 \text{ kWh} \cdot \text{kg}^{-1}$ (originally $1.803 \text{ MWh} \cdot \text{ton}^{-1}$ when related to CO_2 as reported in [17]). A1.1 alternative exhibits the highest consumption of steam by unit of mass of FA $401 \text{ MJ} \cdot \text{kg}^{-1}$, as the FA concentration

is lower than the concentration reached by the other references (A1.2 and A1.3 alternatives). As it was mentioned above, surpluses of renewable energy from PV solar energy were supposed to be used for supplying energy to ER, pumping, and compression. The wide range of consumption of steam per mass unit of FA (from $401 \text{ MJ} \cdot \text{kg}^{-1}$ to $25.7 \text{ MJ} \cdot \text{kg}^{-1}$) highlights the significance of the purification step. As it was expected, the higher FA concentration at the outlet of the ER cell, the lower steam consumption (A1.3 scenario).

3.2. Carbon Footprint of the Selected Alternatives

After a proper LCI was available for each individual case of production of FA, the CF calculations were accomplished with the values of the resources obtained in each alternative. It is worth mentioning that no direct emissions from the ER process are considered. Also, it must be highlighted that the CF calculation was run only for the A1.1, A1.2, and A1.3 alternatives, as the CF values for A_{CONV} and A_{JCR} were provided by the corresponding references [6,7,27]. Ecoinvent database was used to obtain the CO_2 equivalent emissions for the requested resources such as conventional FA production, H_2O , H_2 , O_2 , and steam [27], and the CO_2 equivalent emissions for the requested PV solar energy were based on the results of a previous study [31]. The CO_2 used as feedstock was considered not to contribute to the CF, as all the emissions are allocated to the corresponding main product, which can be electricity in the case of a coal-fired power plant. Figure 3 displays the CF values corresponding to each alternative, considering the next 5 resources: (i) steam for purification; (ii) avoided emissions from the byproduct O_2 ; (iii) avoided emissions from the byproduct H_2 ; (iv) electricity as PV solar energy for the reactor, the pumping, and the compression/liquefaction of H_2/O_2 ; and, finally, (v) the ionized water as raw material, using a functional unit of 1 kg of FA as reference, considering that the FA is at a concentration of 85% wt. The mass of CO_2 per mass unit of FA was excluded from the use of resources, but in any case, it would represent a value of $-1 \text{ kg} \cdot \text{kg}^{-1}$. The CF of the electrode materials and catalysers were neglected, as their lifetimes were assumed to be long enough.

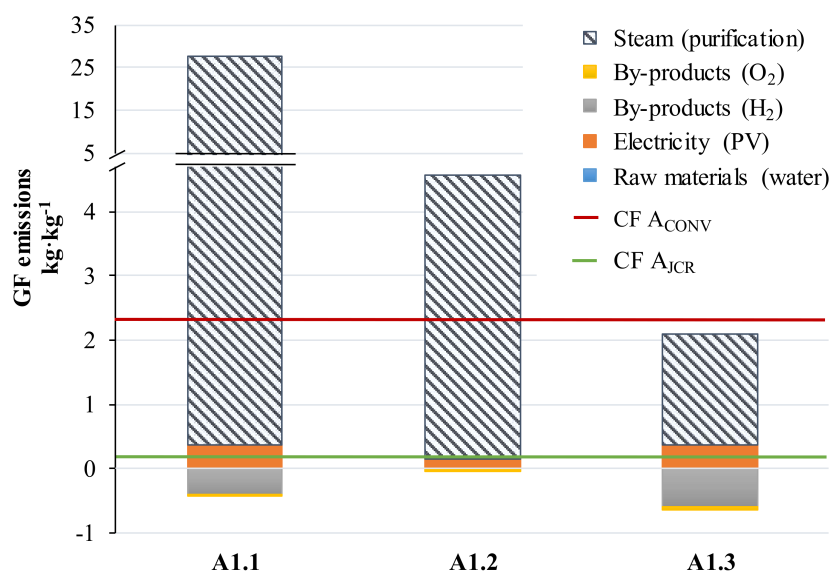


Figure 3. CF values for the selected scenarios (functional unit is 1 kg of FA at a commercial concentration of 85% wt).

It can be observed that the demand of steam for the purification stage is the main contribution to GHG in all cases. However, there is a noticeable difference between A1.1 and both A1.2 and A1.3. It should be remarked that in the case of A1.1, the concentration of FA in the inlet feed to the distillation column was only 1.6% wt., while in cases A1.2 and A1.3 it was feed to the distillation column a FA concentration of 10% wt. and 21% wt., respectively. The CF values as kg of CO_2

per kg of FA obtained for A1.1, A1.2, and A1.3, were $31.9 \text{ kg}\cdot\text{kg}^{-1}$, $5.3 \text{ kg}\cdot\text{kg}^{-1}$, and $1.6 \text{ kg}\cdot\text{kg}^{-1}$, respectively. The scenarios used for comparison, A_{CONV} , and A_{JCR} , present CF values of $2.2 \text{ kg}\cdot\text{kg}^{-1}$ and $0.16 \text{ kg}\cdot\text{kg}^{-1}$, respectively [7,27]. Additionally, it was mentioned above that CF of A_{CONV} could decrease up to $2.07 \text{ kg}\cdot\text{kg}^{-1}$ whether PV solar was supplied to the plant instead of electricity from the production mix. It must be taken into consideration that in the alternative A_{JCR} , H_2 needed in the process is supplied by water electrolysis; therefore, in its CF value ($0.16 \text{ kg}\cdot\text{kg}^{-1}$), there is no explicit mention of the contribution of conventional H_2 production. If a conventional process was used for H_2 production, it would be necessary to add its CF. The CF value, expressed as the mass of CO_2 emitted per kg of H_2 produced, represents a value of $1.7 \text{ kg}\cdot\text{kg}^{-1}$ [27]. Adding $0.102 \text{ kg}\cdot\text{kg}^{-1}$ as CF would lead to a total value of $0.26 \text{ kg}\cdot\text{kg}^{-1}$. The small contribution of hydrogen is related to the use of just 1.38 times the stoichiometric amount of H_2 . In the cases of ER, the avoided burdens from the recovery of H_2 and O_2 have only a significant effect on A1.3. Values displayed in Figure 3 present positive values due to those resources positive CF contributions and negative values from the avoided H_2 and O_2 .

As it was mentioned, the ER of CO_2 to FA has also a positive effect in terms of environmental sustainability: a reduction in the consumption of raw materials is also expected. An assessment of the amount of raw materials needed was carried out in the A_{CONV} , A_{JCR} , and A1.3 scenarios. Table 4 shows the quantities of raw materials needed for the production of 1 kg of FA. For a fair comparison, electricity was assumed to be obtained from renewable energy in all scenarios. While for A_{CONV} scenario, direct figures of heavy oil and natural gas were provided, data for A_{JCR} scenario were derived based on the heating needs obtained from liquefied natural gas (LNG) combustion ($54.40 \text{ MJ}\cdot\text{kg}^{-1}$) [32]. From the point of view of natural resources consumption and their environmental implications, as in the case of conventional fossil fuel utilization, the conventional/commercial fabrication of FA used as benchmark presents higher consumption of natural gas and heavy fuel oil in comparison with both A1.3 and A_{JCR} alternatives. Conventional production of 1 kg FA requires the consumption of natural gas for heating purposes of $0.246 \text{ kg}\cdot\text{kg}^{-1}$, which is in the same order of magnitude than the values of natural gas for heating of both A_{JCR} and A1.3. However, it must be taken into account that the conventional FA route of hydrolysis of methyl formate, which is obtained by carbonylation of methanol, involves a second consumption of natural gas at high pressure for production of the methanol [27]. This additional consumption of natural gas per kg of FA represents an overall consumption of natural gas higher than both CO_2 valorisation options. In addition, conventional production of 1 kg of FA from MeOH and CO involves a consumption of catalysts per unit of mass of FA of $15.6 \times 10^{-6} \text{ kg}\cdot\text{kg}^{-1}$ (such as aluminium oxide, copper oxide, molybdenum, nickel, and zinc) as sourced from Ecoinvent data [27]. In the A_{JCR} scenario, $3.75 \times 10^{-6} \text{ kg}$ of ruthenium and phosphine-based catalysts are reported to be consumed per kg of FA produced [7]. In the case of A1.3, $14.88 \times 10^{-6} \text{ kg}$ of catalysts are needed for the production of 1 kg of FA. Alternative A_{JCR} needs 0.060 kg of H_2 per kg of FA that is produced. In the study, it was assumed that H_2 came from an in-situ electrolyser. However, in a worst scenario, hydrogen would be produced conventionally at refineries by (i) steam reforming of light ends or natural gas (the most common production route in Europe); (ii) partial oxidation (gasification) of heavy oil fractions (produces syngas, from which hydrogen can be separated; and (iii) coal or coke gasification, representing additional fossil fuel consumption in the alternative A_{JCR} .

Table 4. Consumption of raw materials (per unit of kg of FA).

Raw Materials Consumption				
	Unit	A_{CONV} [27]	A1.3	A_{JCR}
Heavy fuel oil	kg	0.405		
Natural gas (<i>heat</i>)	kg	0.273	0.423	0.166
Natural gas at high pressure *	kg	1.250		
Hydrogen	kg			0.060 **

* At 60 bar, 15°C , the natural gas density used is $48 \text{ kg}\cdot\text{m}^{-3}$ (original value was expressed as m^3); ** in the original reference, $90 \text{ kg}\cdot\text{h}^{-1}$ of H_2 is used to produce $1500 \text{ kg}\cdot\text{h}^{-1}$ of FA.

3.3. Remaining Challenges

CO₂ valorisation technologies for production of FA are attractive options that can potentially reduce both the greenhouse effect and the depletion of fossil resources for industrial processes. However, it is still necessary to further improve some technical aspects to produce FA at higher concentrations. This fact must be enough to decrease the high demand of steam in the purification stage that can finally neutralise the CF values with respect to the conventional production process (A_{CONV}) attracting an industrial interest in a more sustainable process. Using renewable energy is another one of the most important approaches to achieve an even carbon cycle. However, in most cases, the high demand of steam in the purification stage overlaps the use of renewable energy, no matter if PV solar or wind energy is used. A future challenge also includes the fact that the steam could come also from a renewable source.

On one hand, it has been already demonstrated that in the alternative of homogeneous catalysts, hydrogen synthesis is the weak spot [6]. It should be further studied and optimised, as it would be one of the main contributors to the high environmental costs through electricity consumption (indirect emissions).

On the other hand, ER, which is at lower level of development, needs further improvement of its energetic efficiencies that are achieved at higher FE values. Some factors such as catalysts, electrodes, electrolytes (composition and pH), and cell configuration could be further improved [19] for better efficiencies. In fact, during the past decades, efforts have focused on the development of metal catalyst. Pb, Hg, In, Sn, Cd, and Tl are metals generally used to produce FA [33]. N-doped porous carbon materials insulating with polymer binders, such as Nafion or PVDF, are commonly used. This is an attractive option due to their low cost, large surface areas, metal-free nature, chemical stability, tunable conductivity, and electrochemical activity [34]. New developments based on dendritic copper-indium alloys have demonstrated their capability at enhancing the control over the product distribution being an inexpensive and efficient option for the production of fuels [35]. It is known that competing H₂ evolution reaction by N-doped carbons in water is sluggish and kinetically negligible under appropriate conditions. In recent years, the use of solid polymers electrolytes has been presented as a powerful alternative to overcome electrode corrosion and the lifetime increase [36]. Yang et al. 2017 demonstrated that an unsuitable choice of the cation exchange membrane may be a significant potential source of FE loss in the formic acid cell [14]. Nafion 324 membrane was the preferred membrane, as is shown in the lowest transport of formate ions into the anode (cases S2 and S3). Finally, an efficient mode of operation of the electrolytic reactor, such as recirculation mode, is necessary to achieve at least an FA concentration of 20% wt. to obtain an even CF compared to the FA conventional process.

4. Conclusions

CO₂ utilisation techniques for the production of FA have been demonstrated to be attractive alternatives compared to the fossil-dependant routes. They show potentially similar CF values and a net replacement of the consumption of fossil fuels under proper future technical developments. This study shows two CCU options at different technological readiness levels. The results displayed that the alternative of ER of CO₂ to FA can be redesigned to provide even CF values compared to commercial production processes, including a reduction in the consumption of raw materials of fossil origin in the whole supply chain. This means that a noticeable increase in the concentration of the HCOOH at the ER reactor is needed. Utilization of renewable energy such as PV solar energy is one of the most important restrictions for achieving production of FA with a more even CF value than the conventional production route of FA; however, the contribution of the CF of the electricity from the PV solar is still dwarfed by the CF derived from the high requirement of steam in the purification stage in order to reach commercial purity (heating for distillation sourced mainly from the combustion of natural gas). The optimization of the electrolytic reactor is still needed in the common ER configurations. An increment of FA concentration in the outlet stream of ER reactor up to 21% wt. demonstrated even steam consumption with respect to the conventional process of FA production.

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